4

APPLICATION OF SIGN RELATIONS IN THE CASE OF 4, 1, 3-CHLORO-DINITRO-BENZENE

E. M. GOPALAKRISHNA

Indian Association for the Cultivation of Science, Calcutta-32, India

(*Received, February* 11, 1960)

The method of systematic application of sign relations as developed and described by Grant, Howells and Rogers (1957) was tried for the sign determination of the structure factors of (*okl*) reflections from (4 : 1 : 3) chloro-dinitro-benzene and found to be very successful

(4 : 1 : 3) chloro-dinitro-benzene (α-modification) belongs to orthorhombic space group Pccn D^{10}_{2h} with $a = 8.96$, $b = 11.08$, $c = 15.73$ Å and with eight molecules per unit cell [Gopalakrishna (1959)]. The (100) projection is of pmg symmetry

Of the 96 observed $|F(okl)|$'s, 40 with larger $|U|$ values were used in the process which gave rise to 300 distinct triple sign relations of the type

$$S(h')\,S(h-h')\approx S(h)$$

and about 100 sign concidences from different pairs of triple sign relations of the type

$$S(A)\,S(B)\,S(C_1)\approx +1$$
$$S(A)\,S(B)\,S(C_2)\approx +1$$

The signs of seven structure factors (of k = even l = even) were obtained from the sign relation of the type

$$S(o,\,2k,\,2l)\approx S(okl)\,S(o\bar{k}\bar{l}) = +1$$
$$S(o,\,2k,\,o)\approx S(okl)\,S(okl) = (-1)^k$$
and
$$S(o,\,o,\,2l)\approx S(okl)\,S(o\bar{k}l) = (-1)^l$$

Starting with the signs of these seven structure factors and using the sign concidences, all the forty terms were assigned signs. The iterative process corrected 13 signs out of those 40 after four cycles of the process, when all the signs were consistent with each other. The electron density map calculated with these forty factors gave out the position of chlorine atom and the approximate orientation of the molecule. Later, the signs of another 15 terms were determined from the triple sign relations. When the contribution due to these fifteen terms was added to the previous map, the approximate positions of all the atoms became

evident. Using these positions and calculating the structure factors, the *R*-value was about 0.40. Fig. 1 shows the electron density synthesised with 90 terms. When the structure factors were calculated using the atomic co-ordinates from this figure, only one was found to be not correct among the previously determined 55 signs.

The $|U|$ values were calculated from intensities measured by visual comparison and were on an arbitrary scale. They were not corrected for absorption nor for temperature effect

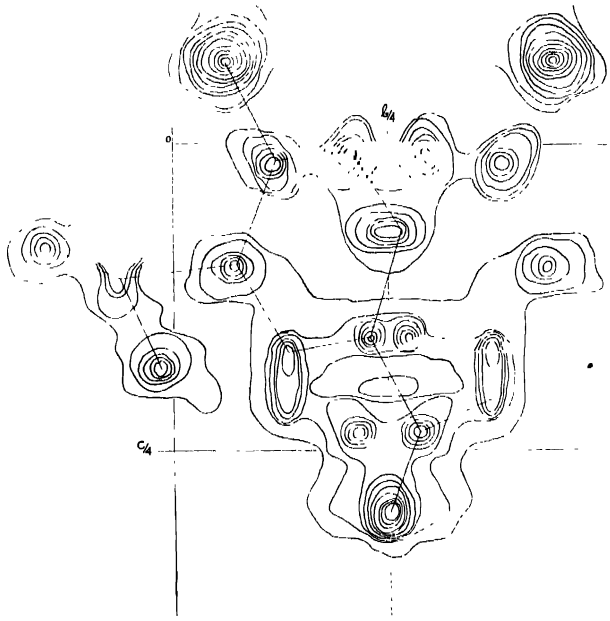

Fig. 1. Electron density map (100) projection calculated with 90 terms

The results obtained in this case show that the method under favourable conditions yields a tentative solution even without any previous knowledge of the stereo chemistry of the molecule or of any signs of the structure factors.

The presence of the chlorine atom among the lighter ones does not prevent the method from yielding a solution. The random and systematic errors in $|U|$ values do not seriously affect the sign determination by this method.

TABLE I

y and *z* co-ordinates of atoms (without refinement)

	y/a	*z/c*		*y/a*	*z/c*
Cl	.063	− 070	C	208	007
C	.117	017	N	.263	.233
C	067	.103	O	.250	.300
			O	.371	.210
C	133	.175	N	− 054	.113
C	.229	163	O	− 017	.183
C	.241	.075	O	− 154	.068

The complete structure analysis after refinement will be published later.

The author wishes to express his deep indebtedness to Prof. B. N. Srivastava, D.Sc., F.N.I., for his keen interest and valuable discussions. He expresses his gratefulness to Dr. B. V. R. Murty for suggesting this work and guiding.

REFERENCES

Grant, D. F., Howells, R. G and Rogers, D., 1957, *Acta Cryst.*, **10**, 489
Gopala Krishna, E. M., 1959, *Zeit. f. Krist.*, **111**, 159